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The study of supramolecular structure of asphaltenes by atomic force microscopy

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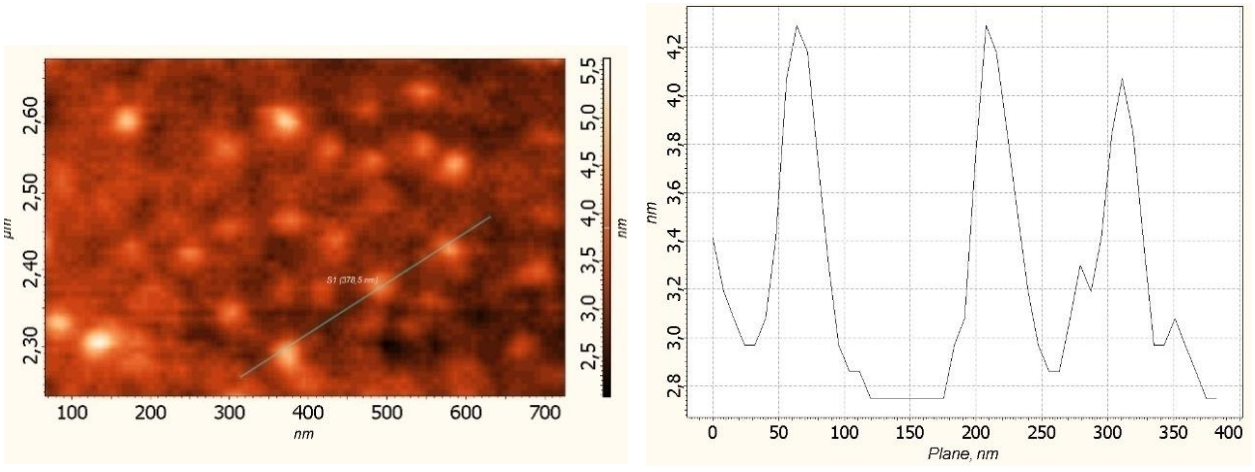
Recently, much attention has been paid to works in which organic materials are used as materials for electronics. This is due to the unique properties of the elements of organic electronics which demonstrate semiconductor and even metallic properties and the sizes of these elements can be comparable with the sizes of an organic molecule [1-3]. Asphaltenes are the prospective structural materials in molecular electronic. It is known that asphaltenes in oil dispersed systems are in the form of supramolecular structures with the size of 1 to 1000 nm, which allows us to consider asphaltenes as the perspective object of nanotechnology. At present, the properties of asphaltenes at the supramolecular level are studied by various physical, physicochemical methods and methods of mathematical modeling [4,5].

Asphaltenes are the high-molecular non-hydrocarbon component of oil, consisting of 90-95% of the hydrocarbon. Asphaltene also includes sulfur in addition to carbon, hydrogen, oxygen and nitrogen. [6]. Large number of experiments were conducted to determine the structure and properties of asphaltenes. In 1961, T. Yen proposed the so-called chain-packed model of the structure of "plate to plate" type asphaltene [7]. Asphaltenes have an increased tendency to associate and form liquid crystal or supramolecular structures. Therefore, the important issue is to determine the degree of molecule association in solution.

Aasphaltenes isolated from the rest of the thermal cracking were used as the objects of the study. The mica was chosen as the substrate because it has an atomically smooth surface. The initial task was to find the optimal concentration of asphaltenes in toluene –the working solution for the next preparation of samples suitable for AFM studies. The working solutions with a concentration of 0.1 g/l were prepared by calculating the mass ratio of asphaltene in the toluene volume. Langmuir-Blodgett technique was used to obtain a monomolecular film of asphaltenes. After trying each of the four standard Langmuir-Blodgett techniques, we used up-draw process of the mica substrate through the film, whereby we obtained the highest quality AFM images. The supported asphaltenes thin film was dried in the Petri dish for 60 minutes at the temperature of 24°C. The resulting sample was studied in tapping mode of an atomic force microscopy by Ntegra-Aura probe nanolaboratory (NT-MDT Company, Russia).

The AFM image (Fig. 1a) shows the topography of the monomolecular layer of asphaltenes. Individual disc-shaped objects are observed on it.



(a) (b)

Figure 1. (a) AFM image of asphaltenes film, (b) cross-section profile along the line marked at (a).

For detailed analysis, a cross-section has been carried out along the line shown in Figure 1a. The cross-section covers 3 separate objects. According to the cross-section profile (Fig. 1b), it can be calculated that the first object has height of 1.3 nm and width of 30 nm. The height of the second object is 1.35 nm and width 30 nm. The third object has height of 1.2 nm and width of 30 nm. Thus, the results of AFM studies show disc-shaped structures constructed from associates of asphaltene molecules. Considering that the size of one molecule does not exceed 3 nm, it can be assumed that the disk-shaped structure consists of about 15-20 molecules. When comparing our experiments results with the results of studies and modeling by Ese et al. [8] and Korzhova et al. [9], it can be assumed that the investigated aggregates have a disk-shaped structure and these structures are similar to discotic liquid crystals.

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